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Flexible dye-sensitized solar cell based on PCBM/P3HT heterojunction

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Using blend heterojunction consisting of C_{60} derivatives [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) and poly(3-hexylthiophene) (P3HT) as charge carrier transferring medium to replace I_3^-/I^- redox electrolyte, a novel flexible dye-sensitized solar cell (DSSC) is fabricated. The characterization of infrared spectra and ultraviolet-visible spectra shows that the PCBM/P3HT heterojunction has not only the absorption in ultraviolet light for PCBM, but also the absorption in visible and near infrared light for P3HT, which widens the photoelectric response range for DSSC. The influence of PCBM/P3HT mass ratio on the performance of the solar cell is discussed. Under 100 mW cm^{-2} (AM 1.5) simulated solar irradiation, the flexible solar cell achieves a light-to-electric energy conversion efficiency of 1.43%, open circuit voltage of 0.87 V, short circuit current density of 3.0 mA cm^{-2} and fill factor of 0.54.

flexible solar cell, dye-sensitized, poly(3-hexylthiophene), [6,6]-phenyl-C61-butyric acid methyl ester

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Since the prototype of a dye-sensitized solar cell (DSSC) was reported in 1991 [1] by O'Regan and Gratzel, it has aroused intensive interest over the past decade due to its low cost and simple preparation procedure. Much effort have been devoted to the improvement of the performance of DSSCs, such as, the modification of titania film electrode [2,3], electrolyte optimization [4–6], etc. Recently, flexible DSSCs based on polymer substrate attracted considerable research attention [7,8] because of its low-cost, light-weight, flexiblity and feasible shape design.

Another important progress in solar cell is polymer solar cell in the 1990s. An important breakthrough came with the introduction of a blend polymer heterojunction of an electron-donor and electron-acceptor as active layer by Sariciftci et al. [9]. This new kind of polymer solar cells has attracted considerable research attention because of its ease of processing, design, large area production, and low-cost [10–12]. In the past decade, in order to improve the performance of polymer solar cells, considerable attempts have been made in the synthesis of conductive polymer materials [13–15], optimization of conductive photoactive layer [16,17], etc. Currently, typically blend heterojunction of poly(3-hexylthiophene) (P3HT) and C_{60} derivatives 6,6-phenyl-C_{61}-butyric acidmethyl ester (PCBM) become a new hot spot in polymer solar cell. P3HT usually is used in electron donor and has higher hole mobility (10^{-4}–10^{-2} cm^2 V^{-1} s^{-1}) and excellent environmental stability [16,18,19]. PCBM is an excellent electron acceptor which has better electron transfer ability and higher electron affinity.

In this paper, P3HT and PCBM are used as donor and acceptor, a D/A heterojunction is prepared accoding to their good solubility, using PCBM/P3HT heterojunction as carrier transferring medium to replace I_3^-/I^- redox electrolyte, a novel flexible TiO_2/dye/PCBM/P3HT dye-sensitized solar cell is fabricated by using low-temperature film-forming technique. The heterojunctionof P3HT/PCBM can not only

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transfer charge carrier, but also harvest incident light, consequently, it is expected that the photoelectric performance of the solar cell can be improved. The flexible DSSC achieves a light-to- electric energy conversion efficiency of 1.43% under 100 mW cm^{-2} (AM 1.5) simulated solar irradiation.

1 Experimental

1.1 Materials and instruments

Poly-(3-hexylthiophene) (P3HT, purity 99.95%) and [6, 6]-phenyl-C61-butyric acid methyl ester (PCBM, purity 99.95%) were purchased from Luoyang Microlight Material Technology Co., Ltd, China. The structure of P3HT and PCBM are shown in Figure 1. TiO_2 nanoparticles (P25) was purchased from Degussa, Germany. 1,2-dichlorobenzene (CB), anhydrous ethanol, isopropanol, nitric acid, acetic acid, tetrabutyltitanate and titanium tetrachloride ($TiCl_4$) were analytic purity grade and purchased from Shanghai Chemical Agent Ltd, China. Sensitizing dye N719 cis-di(thiocyanato) N,N′-bis(2,2′-bipyridyl-4-carboxylic acid-4′-tetrabutylammonium carboxylate) ruthenium(II) was purchased from SOLARONIX, SA. Polyethylene glycol with average molecular weight 20000 (PEG-20000) and Triton X-100 were purchased from the same company. All reagents were used without further treatment before using. Conductive flexible plate (ITO/PEN flexible, sheet resistance 12 Ω cm^{-2}, purchased from Japan) was used as a substrate for precipitating TiO_2 porous film and was cut into 1 cm×2 cm sheets, Pt–ITO/PEN (sheet resistance 5 Ω cm^{-2}) also purchased purchased from Japan.

1.2 Preparation of dye-sensitized TiO_2 film

A certain amount of TiO_2 powder (P25) was pretreated by heating at 450°C for 30 min in an Electric Muffle Furnace), then cooling to room temperature [20]. The treated P25, distilled water and absolute ethanol were mixed with mole ratio of 1∶1∶5 and turned to an autoclave (packing volume <80%) followed by a hydrothermally treatment at 200°C for 24 h, then cooling in room temperature, thus a homogeneous and stable TiO_2 colloid was obtained. ITO/PEN substrate was immerged in a 50% ethanol solution for 24 h, and then the substrate was cleaned with 95% ethanol for several times. The cleaned substrates were kept in absolute ethanol and blow dried prior to use.

The TiO_2 colloid was coated on the ITO/PEN substrate by a doctor-scraping technique. The thickness and the area (about 0.5 cm × 0.4 cm) of TiO_2 film was controlled by the adhesive tape around the edge of the cleaned ITO/PEN substrate [21,22]. The process was repeated for three times to form a thick TiO_2 film. The film was dried in moisture-free air and was irradiated for 15 min [23,24]. The resultant TiO_2 flexible film was heated at 100°C for 30 min in air. Finally, the TiO_2 flexible film was immersed in a 2.5×10^{-4} mol L^{-1} dye N719 absolute ethanol solution for 24 h to adsorb the dye adequately, then the dye-sensitized TiO_2 film was washed and dried in moisture-free air. Thus a flexible TiO_2 film electrode was obtained.

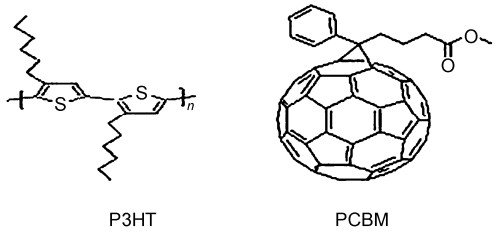

Figure 1 Schematic diagram of PCBM and P3HT.

1.3 Preparation of flexible dye-sensitized solar cell

PCBM and P3HT were mixed with a predetermined mass ratio and dissolved in 1,2-dichlorobenzene solvent to form a conductive polymer solution with the concentration of 15 mg/mL, under stirring at 40°C for 24 h. A dye-sensitized solar cell was assembled by injecting PCBM/P3HT solution into the aperture between the TiO_2 porous film electrode (anode electrode) and a Pt-ITO/PEN (cathode electrode). The two electrodes were clipped together and a cyanoacrylate adhesive was used as a sealant to prevent the polymer solution from leaking. Then the cell was placed overnight at room temperature to allow PCBM/P3HT penetrate into the aperture of TiO_2 nanoporous film completely. The schematic diagram of TiO_2/dye/PCBM/P3HT flexible solar cell is shown as in Figure 2.

1.4 Measurements

Fourier transform infrared (FTIR) spectra of samples were measured using a Nicolet Impact 410 FTIR spectrometer. The UV-Vis absorption spectra of samples were measured on an Optizen (3100 UV) spectrophotometer.

The photovoltaic test of the dye-sensitized solar cell was carried out by measuring photocurrent-photovoltage (*J*-*V*) character curves under irradiation of white light from a 100 mW cm^{-2} (AM 1.5) with a solar simulator (XQ-500W, Shanghai Photoelectricity Device Company, China) and a computer controlled voltage current source-meter CHI660C electrochemical measurement system. The incident light intensity and the active cell area were 100 mW cm^{-2} and 0.5 cm^2, respectively. The fill factor (*FF*) and the overall light-to-electrical energy conversion efficiency (η) of the

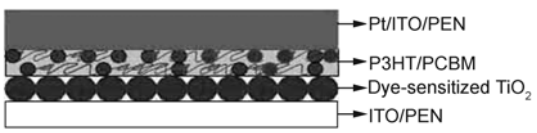

Figure 2 Schematic diagram of TiO_2/dye/PCBM/P3HT flexible DSSC.

solar cell were calculated according to the following equations:

$$\eta\ (\%) = \frac{V_{\max} \times J_{\max}}{P_{\text{in}}} \times 100\% = \frac{V_{\text{OC}} \times J_{\text{SC}} \times FF}{P_{\text{in}}} \times 100\% \ , \quad (1)$$

$$FF = \frac{V_{\max} \times J_{\max}}{V_{\text{OC}} \times J_{\text{SC}}}, \quad (2)$$

where J_{SC} is the short-circuit current density (mA cm^{-2}), V_{OC} is the open-circuit voltage (V), P_{in} is the incident light power and J_{max} (mA cm^{-2}) and V_{max} (V) are the current density and voltage at the point of maximum power output in the *J-V* curves, respectively.

2 Results and discussion

2.1 FTIR spectra

The Fourier transform infrared (FTIR) spectra of PCBM, P3HT and PCBM/P3HT hybrid were measured and shown in Figure 3. Curve a in Figure 3 is for PCBM sample, the absorption peak at 1740 cm^{-1} is the characteristic peak of C=O group, the peak at 1080 cm^{-1} belongs to the O-CH_3 stretching vibration, the absorption bands at 2855 and 2940 cm^{-1} attribute to the -CH_2 stretching vibration. The peak at 760 cm^{-1} is related to the bending vibration of Ar-H. The four peaks at 1428, 1189, 573 and 524 cm^{-1} are typically characteristic peaks for Fullerene [25]. The peak at 524 cm^{-1} is related to fingerprint. The curve a shows the being of [6, 6]-phenyl-C_{61}-butyric acid methyl ester (PCBM).

Curve b in Figure 3 is for P3HT, the absorption peaks at 3097 and 2853–2952 cm^{-1} are for the C-H bond stretching vibration on thiophene ring, the peaks at 1460–1580 cm^{-1} is the stretching vibration of C=C bond, the peak at 1380 cm^{-1} is the stretching vibration for CH_2, the peak at 825 cm^{-1} is the bending vibration of C-H bond. The peak at 725 cm^{-1} is the characteristic absorption of S atom on polythiophene ring.

Curve c in Figure 3 is the infrared spectrum of the hybrid PCBM/P3HT with PCBM/P3HT ratio at 1∶2. From the curve, all characteristic absorption peak locations for PCBM and P3HT do not change after PCBM blends with P3HT. The characteristic absorption peak intensity for Fullerene becomes smaller, the peak at 1428 cm^{-1} is concealed, the peak at 1740 cm^{-1} for C=O group becomes smaller, which is due to the formation of hydrogen bond for C=O···H^{+}···S^{2-}, the electron of C=O transferring to S atom, and decreasing the electron cloud density of C=O. The stretching vibration peaks at 3097 and 2853–2952 cm^{-1} are for the C-H bond on thiophene ring, the stretching vibration peak at 1460–1580 cm^{-1} is for C=C bond, and the stretching vibration peak at 1380 cm^{-1} for CH_2 bond become wider and weaker. The bending vibration peak at 825 cm^{-1} for C-H bond does not change. The characteristic peak for S atom on polythiophene ring at 725 cm^{-1} becomes larger and wider. The FTIR spectrum indicates the formation of a blend heterojunction PCBM/P3HT without new compound formation.

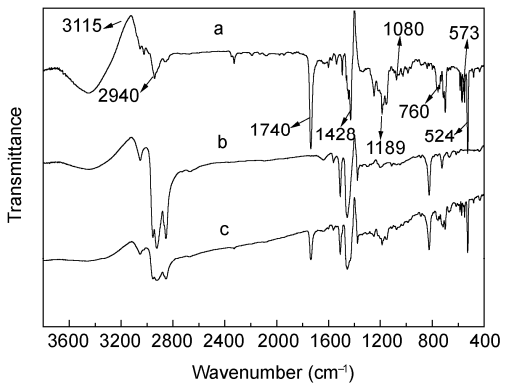

Figure 3 FTIR spectra of (a) PCBM, (b) P3HT, and (c) PCBM/P3HT.

2.2 UV-Vis absorption spectra

The UV-Vis absorption spectra of the composite films with and without dye sensitized are shown in Figure 4. The PCBM/TiO_2 film, P3HT/TiO_2 film, PCBM/P3HT/TiO_2 film with dye sensitized have a highest absorption band around 520 nm, which is consistent with the absorptions of dye 719. Red-shift can be observed in the absorptions of composite films with and without dye sensitized, which is due to that there is a track forbidden resistance of the spin-spin transition at 410–620 nm for PCBM, increased the scope of hybrid materials absorption [26], and the red-shift is more obvious for the sample dye sensitized. The UV-Vis absorption spectra of PCBM/TiO_2 film with and without dye-sensitized are basically the same before 465 nm are shown in Figure 4(a), while they are different after 465 nm, after dye-sensitizing, the red-shift is over 50 nm for PCBM/TiO_2 film. P3HT/TiO_2 and PCBM/P3HT/TiO_2 dye-sensitized films have the similar change as shown in Figure 4(b) and (c). It can be seen in Figure 4(c) that there is an absorption peak near the 365 nm for the film without dye sensitized, which is due to the PCBM [27], but it disappeared to the film with dye sensitized which may be caused by absorption of dye to the ultraviolet light near 365 nm.

The UV-Vis absorption spectra of dye-sensitized PCBM/TiO_2 film, P3HT/TiO_2 films and PCBM/P3HT/TiO_2 film are shown in Figure 4(d). Comprared to the films without dye sensitized, they have a stronger absorption which affected by the dye in the visible absorption. The UV-Vis absorption spectra indicate that the PCBM/P3HT hetrojunction has not only the absorption in ultraviolet light for PCBM, but also the absorption in visible and near infrared light for P3HT, which widens the photoelectric response range of the DSSCs.

2.3 Influence of illumination on the properties of flexible DSSC

The *J-V* curves and photoelectric parameters of flexible

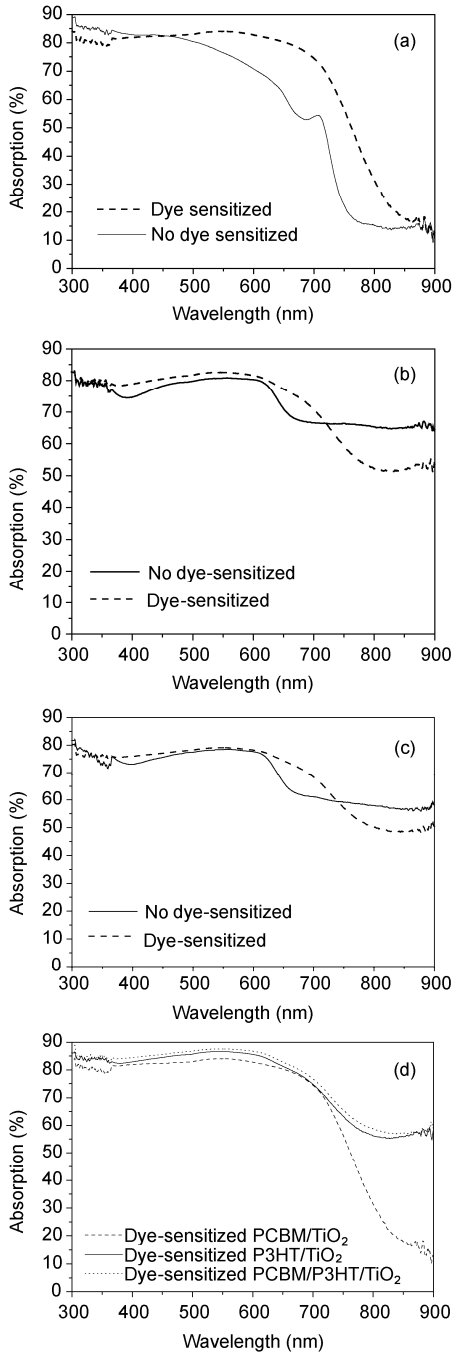

Figure 4 UV-Vis absorption spectra of films. (a) PCBM/TiO_2 film with and without dye sensitized; (b) P3HT/TiO_2 film with and without dye sensitized; (c) PCBM/P3HT/TiO_2 film with and without dye sensitized; (d) dye-sensitized PCBM/TiO_2, P3HT/TiO_2, and PCBM/P3HT /TiO_2 films.

dye-sensitized solar cell with different illumination time are shown in Figure 5 and Table 1, respectively. The open circuit voltage (V_{OC}) and fill factor (*FF*) slightly decrease with the increase of illumination time. And the short circuit current density (J_{SC}) increase with the illumination time increase. When the illumination time is 1.5 min, the photoelectric conversion efficiency reaches a steady highest of 1.43%. This is because with the increase of the illumination

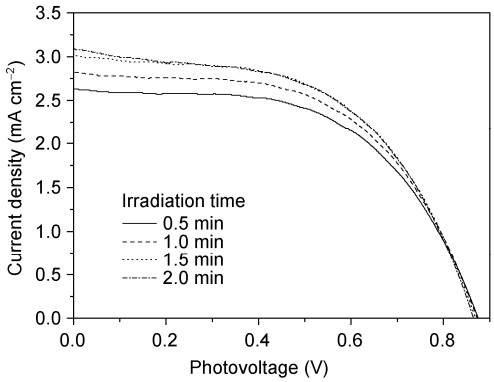

Figure 5 *J-V* curves for DSSCs with different illumination time.

Table 1 The photoelectric parameters for flexible DSSC with different illumination time

Irradiation (min)	V_{OC} (V)	J_{SC} (mA cm^{-2})	*FF*	η (%)
0.5	0.88	2.62	0.56	1.29
1.0	0.87	2.82	0.55	1.34
1.5	0.87	3.02	0.54	1.43
2.0	0.86	3.09	0.53	1.41

time the temperature of the flexible solar cell increase, which result in the improvement of charge carriers transferring in D/A system. Also, with the increase of temperature, the polymer free volume increases, which improves further transfer of charge carriers. The open circuit voltage mainly depends on the cell composition. Since the composition is the same for different illumination time, the V_{OC} changes a little.

2.4 Influence of P3HT/PCBM ratio on the performance of flexible DSSC

In order to evaluate the effect of P3HT/PCBM in the solar cell, the *J-V* curves for the DSSC with different P3HT/PCBM mass ratio were measured under standard light irradiation and shown in Figure 6, and photoelectric parameters are summarized in Table 2. From the Table, PCBM/P3HT

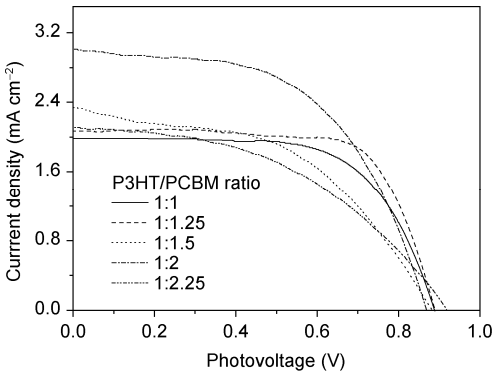

Figure 6 *J-V* curves for DSSCs with different mass ratio.

Table 2 Photoelectric parameters for the flexible DSSC with different P3HT/PCBM mass ratio

P3HT/PCBM (mass ratio)	V_{OC} (V)	J_{SC} (mA cm^{-2})	*FF*	η (%)
1∶1	0.89	1.9	0.45	0.79
1∶1.25	0.89	2.1	0.71	1.31
1∶1.5	0.88	2.4	0.48	0.99
1∶2	0.87	3.02	0.54	1.43
1∶2.25	0.90	2.1	0.42	0.88

mass ratio has a great influence on the photoelectric performance of the flexible DSSC.

PCBM/P3HT hybrid absorbs photons and produces excitons under light irradiation, the excitons are transported to the D/A heterojunction. Owing to different electronic affinity for two components (PCBM and P3HT) in the D/A heterojunction, the excitons are inducied and separated into electrons and holes, and then are transported to the corresponding electrodes. The heterojunction facilitates the separation of excitons, accelerate s the trasferring of charge carriers, and inhibits the recombination between photoinduced electrons an holes greatly, increases photocurrent and photoelectric properties significantly. In addition, the ester bond generated by carboxyl of dye N719 with hydroxyl of TiO_2 film improves the coupling between the TiO_2 conduction band and the π orbital of dye and ready for the electron transferring [28]. When PCBM/P3HT mass ratio is 1∶2, a continuous path of PCBM can be established to make sure the charge carriers are transferred to the electrodes effectively [29–31]. It can be seen from Figure 6 and Table 2 that the flexible DSSC with the PCBM/P3HT mass ratio at 1:2 possesses the best photoelectric performance with a photoelectric conversion efficiency of 1.43%, current density of 3.02 mA cm^{-2} and fill factor of 0.54. The open circuit voltage mainly is determined by the energy gap of donor material HOMO and acceptor material LUMO [28], since the composition is the same for different illumination time, the V_{OC} changes a little.

3 Conclusions

In conclusion, a novel flexible ITO/PEN/TiO_2/dye/PCBM /P3HT dye-sensitized solar cell was fabricated by using blend heterojunction consisted of C_{60} derivatives 6, 6-phenyl-C_{61}-butyric acidmethyl ester (PCBM) and poly(3-hexylthiophene) (P3HT) as charge carrier transferring medium to replace I_3^-/I^- redox electrolyte. The spectra of FTIR, UV-visible absorption spectra showed that the P3HT/PCBM heterojunction widened the incident light harvest range from ultraviolete to visible light, improved the photoelectrical response of dye-sensitized solar cell effectively. Under an optimized condition with PCBM/ P3HT mass ratio at 1∶2, the cell showed a short circuit current of 3.02 mA cm^{-2}, the open circuit voltage of 0.87 V, and fill factor of 0.540 and light-to-electric energy conversion efficiency of 1.43% under 100 mW cm^{-2} (AM 1.5) simulated solar light irradiation.

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